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ARTICLE

# All Inkjet-Printed Piezoelectric Electronic Devices: Energy generators, Sensors and Actuators

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Inkjet printing is considered to be a key technology in the field of flexible electronics due to its capability to deposit different types of materials in a controlled and defined way. However, inkjet printing of functional materials such as the fluorinated piezoelectric copolymer P(VDF-TrFE) still remains a challenge. In this regard, a piezoelectric ink was formulated in a narrow viscosity range compatible with the specific print head used in this work. Characterization of the dielectric, ferroelectric and piezoelectric properties along with the morphology and crystallinity of the film showed excellent agreement with traditional solution processed thin films. Consequently, inkjet printed P(VDF-TrFE) layers were subsequently integrated as functional layer into entirely inkjet printed flexible electronics devices such as energy harvesters, sensors and actuators contributing to the development of flexible electronic applications.

## Introduction

Electroactive polymers are some of the most promising smart materials for flexible electronics. Amongst them, fluorinated polymers based on polyvinylidene fluoride (PVDF), exhibit advanced electroactive properties. These attractive features are further pronounced for the copolymer polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE). The addition of trifluoroethylene (TrFE) modifies the molecular chain arrangement from a trans-gauche-trans-gauche conformation into an all-trans conformation resulting in a β crystalline phase, which is the key to achieving higher polarization level and piezoelectric coefficient. Such remarkable piezo, pyro and ferroelectric characteristics coupled with mechanical flexibility make P(VDF-TrFE) an extremely attractive material in sensing applications, [1-3] and flexible memory cells [4-5].

To date, patterning of P(VDF-TrFE) thin film has been achieved by using standard microelectronics photolithography employing an additional photoresist masking and reaction ion etching $O_2$ plasma [6]. Nevertheless, this micro-structuration approach being limited to wafer-size surfaces requires multiple fabrication steps (deposition, masking, development and cleaning processes) consuming time and materials. To overcome this issue, micromachining approaches that do not require the high-cost semiconductor manufacturing equipment used for silicon microfabrication have been developed recently to realize polymer micro electromechanical systems (MEMS). [7] Although, this approach has led to advanced MEMS [3,8] it does not permit patterning single layers with arbitrary thicknesses. Thus, emerging printing technologies that allow deposition of materials on desired locations without masking with limited material losses are gaining a growing amount of interest due to their potential for the production of cost effective and large-area flexible electrical devices. [9] In particular, inkjet printing offers a maskless and non-contact deposition of materials onto a wide variety of nonplanar surfaces. Recently, printed electronic devices such as radio frequency identification (RFID) tags [10], organic light-emitting diodes (OLED) [11], organic photovoltaics (OPV) [12] and thin film transistors [13,14] have been realized opening the way for future more advanced electronic circuits. Nevertheless, the realization of fully inkjet-printed electronics devices remains challenging mainly due to the complex interplay between a large number of involved parameters like ink viscosity, surface tension of substrate and ink, or drying kinetics. [15,16] Also, organic layer solvent interaction during printing of multilayer structures and the elevated curing temperatures needed for most nanoparticle based metal inks are additional issues that have to be considered for multi-layers printed devices. These aforementioned considerations responsible for limitations in performances and printable functionalities are the main reasons why printed electronics devices have not yet taken a major share on the market of flexible electronics.

In this regard, active matrices of piezoelectric pressure sensors and flexible actuators have been realized entirely from inkjet-printing technology. The fabricated flexible printed electronics sensors and

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actuators exhibited promising physical and electrical properties. This constitutes an advance towards the development of inexpensive large-area flexible electronics applications.

## Results and discussion

### Inkjet printing of P(VDF-TrFE) ink

P(VDF-TrFE) [70:30] inks have been formulated with different P(VDF-TrFE) concentrations as well as the types of solvent or mixture of solvents in order to obtain a uniform thin film without clogging the nozzle head up during jetting. Although cyclopentanone is known to be a good solvent of P(VDF-TrFE), its low density and high volatility characteristics are not suitable for inkjet printing technology. In fact, solvents with high evaporation rate can lead to rapid formation of a solid polymer membrane in the nozzle where ink is in contact with air resulting in clogging of the cartridge. [17] Consequently, cyclopentanone has been mixed with different amount of dimethyl sulfoxyde (DMSO), a solvent having high boiling point and low vapor pressure in order to enable jetting from the nozzle head.

The optimized P(VDF-TrFE) ink formulation that led to reproducible continuous jetting as shown in Supporting Information Figure 1, is described in Table 1. It was obtained for a 1wt. % of P(VDF-TrFE) dissolved in cyclopentanone / DMSO mixture of solvents at a ratio of 50:50. The thicknesses of the deposited layers were measured with a mechanical profilometer (Decktak XT-A from Brucker). The thickness of a single layer was measured to be about 170 nm whereas a total layer of 2 µm was obtained after twelve printing steps. Afterwards, the surface tension and the viscosity of the optimized formulation were characterized. The surface tension of printed P(VDF-TrFE) ink has been determined by contact angle of static sessile drops of water, ethylene glycol and diiodomethane using a goniometer to be 35.6 $mN.m^{-1}$. The viscosity of the ink formulation was characterized using a rheometer Anton Paar MCR302. As expected, the prepared P(VDF-TrFE) ink was found to behave like a Newtonian fluid exhibiting a constant viscosity of 5.4 $mPa.s^{-1}$ (Supporting Information 1). Furthermore, the low contact angle of printed P(VDF-TrFE) ink on silver bottom electrodes was measured to be 9.6° ± 1.3°. This highlights a good wettability of the optimized formulation with the underneath layer, a key requirement for multilayer printed devices.

| PVDF-TrFE ink formulation | |
|---|---|
| Solvent ratio | 50:50 |
| PVDF-TrFE concentration [wt. %] | 1 |
| Viscosity, η [$mPa.s^{-1}$] | 5.4 |
| Contact angle [°] | 9.6 |
| Surface tension [$mN.m^{-1}$] | 35.6 |

Table 1. Optimized P(VDF-TrFE) ink formulation parameters

Secondly, inkjet printing conditions were also optimized in order to obtained high quality inkjet printing. It requires a stable drop formation (single droplet generation for each electrical impulse, without the formation of satellite droplets) and jetting of ink (avoiding deviation of droplet trajectory). Otherwise, unstable jetting may lead to uncontrolled amount of ink deposition on to undesired locations. As shown by the high speed jetting sequence images presented in Supporting Information 2, a stable jetting without the formation of satellite droplets or long filament has been obtained under optimized printing parameters, as listed in Supporting Information Table 1.

Figure 1a and 1b depict the schematic of the fabricated P(VDF-TrFE) based flexible sensors and actuators devices respectively. Figure 1d and 1e are the corresponding optical images of the fabricated devices. Devices were printed using an inkjet single nozzle deposition system Jetlab4 from Microfab. Initially, the bottom electrodes were printed from a silver nanoparticle dispersion from Genes'ink ® onto 50 µm thick polyethylene naphthalate (PEN) substrates using driving voltages of 50 V, a pulse width of 10 µs, a printing frequency of 600 Hz and a droplet spacing of 125 µm. The as-printed bottom electrode layer was dried in a convection oven at a temperature of 100 °C for 60 min. Secondly, the aforementioned optimized P(VDF-TrFE) ink formulation was printed on top of the silver bottom electrode. Driving voltages of 55 V were applied with a pulse width of 16 µs at a printing frequency of 600 Hz and a droplet spacing of 50 µm. The printed P(VDF-TrFE) layers were thermally annealed on a hot plate at a temperature of 140°C for 60 minutes and slowly cooled down to room temperature. Finally, a top electrode was printed using the same conditions as the bottom electrodes. Figure 1c depicts a cross section schematic of the printed sensors and actuators and Figure 1f is an SEM image of the free standing piezoelectric resonator beam.

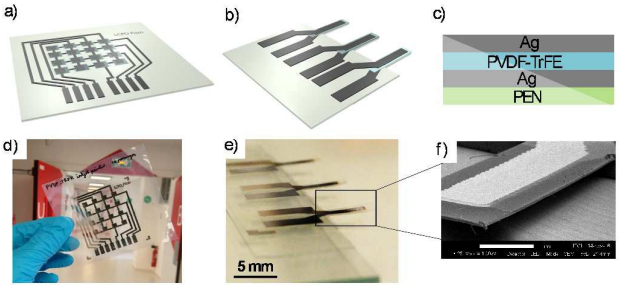


Figure 1. a) Schematic of fabricated flexible inkjet-printed piezoelectric sensor, b) actuator, c) cross section of the printed devices, d) optical image of flexible pressure sensors, e) optical image of the cantilever piezoelectric actuator and f) SEM image of a free-standing piezoelectric cantilever beam

### Characterization of inkjet-printed P(VDF-TrFE) thin film

The dielectric response of the active thin film was recorded using a Solartron SI1260 impedance analyzer. Figure 2a shows the relative permittivity and tan delta of inkjet-printed P(VDF-TrFE) as a function of frequency from 10 Hz to 1 MHz measured at 20 °C. As expected, the experimental data of dielectric constant slightly

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dependent on frequencies and are consistent with classical values obtained from spin coated thin film at room temperature (ε' =12 at 100Hz). The temperature dependence of printed P(VDF-TrFE) copolymer showed that the relative permittivity and losses were quite stable with respect to temperature, maintaining its properties over a range of temperature from 20 °C to 80 °C (Supporting information 3). In agreement with previous report, [18] the DSC of inkjet printed P(VDF-TrFE) film showed the Curie temperature at 69°C upon 1st cooling and 112°C upon 2nd heating. The melting and crystallization temperature were observed at 152°C and 128°C, respectively (Figure 2b). The crystallinity degree of the copolymer was extracted to be 52.6 %.

Intrinsically, P(VDF-TrFE) does not possess a high remanent polarization ($P_r$) and behaves like a normal gate dielectric material. In order to induce piezoelectricity in the P(VDF-TrFE) layer, a poling process is required so that $P_r$ can be generated inside the material. P(VDF-TrFE) is also classified as ferroelectric material which has two or more states with non-zero polarization in the absence of electric field. These polarization states can be switched from one to another by the application of an electric field leading to a hysteresis loop in the polarization versus electric field (P-E) electrical characterization responses as shown by Figure 2c. Herein, a poling electric field of 100 $MV.m^{-1}$ has been applied between the top and bottom Ag electrodes. The coercive fields (± $E_C$) which refer to the minimum voltages required to reverse the ferroelectric polarization, determined as the intersections of the P-E loop with the electric field axis, were measured to be ± 50 $MV.m^{-1}$. The remanent polarizations (± $P_r$) were obtained from the intersections of the loop with the polarization axis and calculated to be approximately ± 7.8 $\mu C.cm^{-2}$. Consistent with previously reported values, [3,8] these values confirmed the efficient polarization of the printed P(VDF-TrFE) thin film. The morphology of the printed piezoelectric film was characterized using a Bruker fast scan atomic force microscopy (AFM). Figure 2d is an AFM surface height scan of a 2 µm thick P(VDF-TrFE) film depicting the crystal grains of P(VDF-TrFE). The average surface roughness was measured to be 3.9 nm.

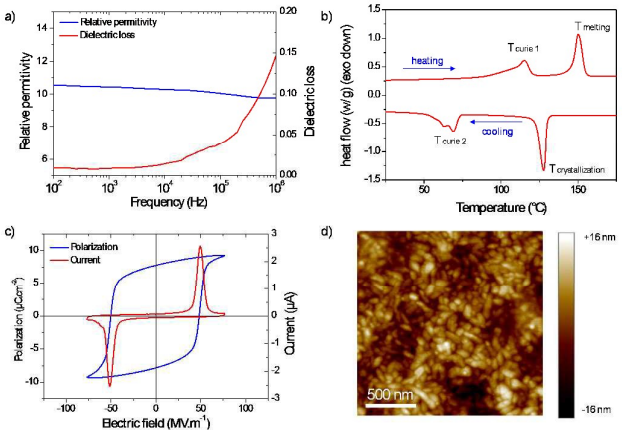


Figure 2. a) Relative permittivity and tan delta of printed P(VDF-TrFE) thin film as a function of frequency from 10 Hz to 1 MHz measured at 20 °C, b) DSC of P(VDF-TrFE), c) polarization versus electric field loop at room temperature and d) AFM image of a 2 µm thick printed P(VDF-TrFE) film

**Inkjet-printed electronics**

To demonstrate the energy generating capability of a 2 µm thick piezoelectric film, its output voltage in response to finger touch were measured in an open circuit voltage configuration with a digital oscilloscope (Agilent DSO-X-2002A). Non-polarized thin films did not show any voltage output, upon being subjected to compressive force by finger pressure. On the contrary, polarized thin films were found to be highly sensitive to human finger touch. The piezoelectric energy generator under applied finger pressure, (estimated to few kPa) generated an average output voltage of 250 mV as shown by Figure 3a. The reproducibility and reversibility of the piezoelectric sensor is illustrated in Supporting Information 4. To further demonstrate its energy generating capability, we set-up a piezo trigger switch circuit by connecting the inkjet-printed piezoelectric device to a CMOS mono stable integrated circuit (NE555P timer) that works with a 5V DC voltage. The module gives a "logic high" when the sensor detects a finger touch pressure. By adjusting the value of the RC time constant component of the CMOS circuit the high signal period can be tuned. Then, a 5 mm yellow LED has been connected to the electronic interface for effective visual observation of the output status (Figure 3c).

In addition, P(VDF-TrFE) based organic resonators have been prepared as shown in Figure 1e and 1f. For electromechanical characterization, the P(VDF-TrFE) based cantilevers were mounted manually on microscope glass slides. Resonance frequencies of the cantilevers were recorded from a laser Doppler vibrometer MSA-500 from Polytec. The spectra of the first out-of-plane flexural mode of resonance measured at 2560 Hz of the fabricated cantilever are illustrated in Figure 3b. The piezoelectric coefficient $d_{31}$ of the inkjet-printed P(VDF-TrFE) layer was extracted from a reported model [8] that relates the tip displacement of the cantilever to its piezoelectric coefficient. The material's properties used in the model to extract the piezoelectric coefficient are listed in Supporting Information 5. A $d_{31}$ value of 10.4 $pm.V^{-1}$ has been calculated to be consistent with previously reported values [8, 19].

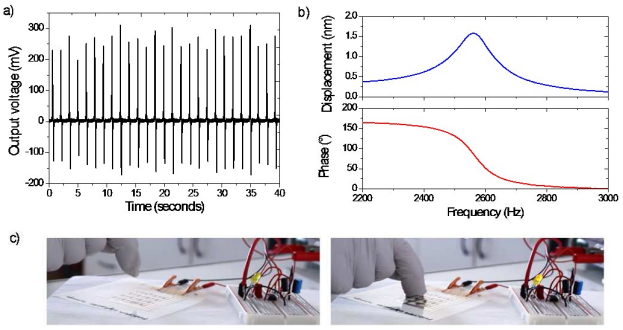


Figure 3. a) Open circuit output voltage generated by the P(VDF-TrFE) thin film in response to finger touch pressure, b) amplitude of displacement and phase spectra of the first out-of-plane flexural mode of resonance of a piezoelectric cantilever resonator and c) images depicting the capability of the inkjet piezoelectric film generated voltage pulse to act as a switch activating the output of the NE555P timer to turn on a yellow LED by a single finger touch

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## Conclusions

In the present work, we have demonstrated inkjet printing of fluorinated polymer P(VDF-TrFE) used as piezoelectric generators and transducers for flexible sensors and actuators devices. The resultant uninform P(VDF-TrFE) thin films exhibit piezo and ferroelectric properties comparable with values reported for spin coated thin films. A remanent polarization of 7.8 $\mu C.cm^{-2}$ and $d_{31}$ piezoelectric coefficient of 10.4 $pm.V^{-1}$ were obtained. The presented entirely inkjet-printed P(VDF-TrFE) based sensors and actuators with such performance contribute to the development of printing electroactive polymer for diverse flexible electronic applications.

## Acknowledgements

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## References

1 S. Khan, S. Tinku, L. Lorenzelli and R. S. Dahiya, Flexible Tactile Sensors Using Screen-Printed P(VDF-TrFE) and MWCNT/PDMS Composites, *IEEE Sensors Journal*, 2015, **6**, 3146

2 M. Zirkl, A. Sawatdee, U. Helbig, M. Krause, G. Scheipl, E. Kraker, P. Andersson Ersman, D. Nilsson, D. Platt, P. Bodö, S. Bauer, G. Domann and B. Stadlober, An All-Printed Ferroelectric Active Matrix Sensor Network Based on Only Five Functional Materials Forming a Touchless Control Interface, *Adv. Mater.,* 2011, **23**, 2069–2074

3 D. Thuau, M. Abbas, G. Wantz, L. Hirsch, I. Dufour, C. Ayela, Piezoelectric polymer gated OFET: Cutting-edge electro-mechanical transducer for organic MEMS-based sensors, *Sci. Rep*., 2016, **6**, 38672

4 D.Thuau, M. Abbas, G. Wantz, L. Hirsch, I. Dufour, C. Ayela, Mechanical strain induced changes in electrical characteristics of flexible, non-volatile ferroelectric OFET based memory, *Org. Electron.*, 2017, **40**, 30-35

5 P. Cosseddu, S. Lai, G. Casula, L. Raffo, A. Bonfiglio, High performance, foldable, organic memories based on ultra-low voltage, thin film transistors, *Org. Electron*., 2014, **15**, 3595

6 T. Sharma, S.-S. Je, B. Gill, J. Zhang, Patterning piezoelectric thin film PVDF–TrFE based pressure sensor for catheter application, *Sensors and Actuators A*, 2012, **177**, 87–92

7 E Lemaire, D Thuau, B Caillard, I Dufour, Fast-fabrication process for low environmental impact microsystems, Journal of cleaner production 108, 207-216

8 P.-H. Ducrot, I. Dufour and C. Ayela, Optimization of PVDF-TrFE processing conditions for the fabrication of organic MEMS resonators. *Sci. Rep.*, 2016, **6**, 19426

9 M. Singh, H.M. Haverinen, P. Dhagat, G.E. Jabbour, Inkjet printing-process and its applications, *Adv. Mater*., 2010, **22**, 673–685

10 V. Sanchez-Romaguera, M. A. Ziai, D. Oyeka, S. Barbosa, J. S. R. Wheeler, J. C. Batchelor, E. A. Parker and S. G. Yeates, Towards inkjet-printed low cost passive UHF RFID skin mounted tattoo paper tags based on silver nanoparticle inks, *J. Mater. Chem. C*, 2013, **1**, 6395-6402

11 H. Zheng, Y. Zheng, N. Liu, N. Ai, Q. Wang, S. Wu, J. Zhou, D. Hu, S. Yu, S. Han, W. Xu, C. Luo, Y. Meng, Z. Jiang, Y. Chen, D. Li, F. Huang, J. Wang, J. Peng, Y. Cao, All-solution processed polymer light-emitting diode displays, *Nat. Commun*., 2013, **4**, 1971.

12 A. Lange, M. Wegener, C. Boeffel, B. Fischer, A. Wedel, D. Neher, A new approach to the solvent system for inkjet-printed P3HT:PCBM solar cells and its use in devices with printed passive and active layers, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1816–1821

13 Y. Xu, C. Liu, D. Khim and Y.-Y. Noh, Development of high-performance printed organic field-effect transistors and integrated circuits, *Phys. Chem. Chem. Phys*., 2015, **17**, 26553-26574

14 G. Mattana, S. Delile, L. Fillaud, B. Piro, V. Noel, All-inkjet-printed flexible Organic Electrochemical Transistors for the detection of biological molecules in liquid media, E-MRS Spring Meeting 2017, Strasbourg (France)

15 C. W. Sele, T. Werne, R. H. Friend, H. Sirringhaus, Lithography-Free, Self-Aligned Inkjet Printing with Sub-Hundred-Nanometer Resolution, *Adv. Mater*., 2005, **17**, 997-1001

16 S. Nau, C. Wolf, K. Popovic, A. Blümel, F. Santoni, A. Gagliardi, A di Carlo, S. Sax, and E. J. W. List-Kratochv, Inkjet-Printed Resistive Switching Memory Based on Organic Dielectric Materials: From Single Elements to Array Technology, *Adv. Electron. Mater*., 2015, **1**, 1400003

17 R. I. Haque, R. Vié, M. Germainy, L. Valbin, P. Benaben, X. Boddaert, Inkjet printing of high molecular weight PVDF-TrFE for flexible electronics, *Flexible and Printed Electronics*, 2016, **1**, 015001

18 G. Teyssedre, A. Bernes, and C. Lacabanne, "DSC and TSC study of a VDF/TrFE copolymer," *Thermochimica Acta*, 1993, **226**, 65–75

19 O. Pabst, J. Perelaer, E. Beckert, U. S. Schubert, R. Eberhardt, A. Tünnermann, All inkjet-printed piezoelectric polymer actuators: Characterization and applications for micropumps in lab-on-a-chip systems, *Org. Electron*., 2013, **14**, 3423-3429

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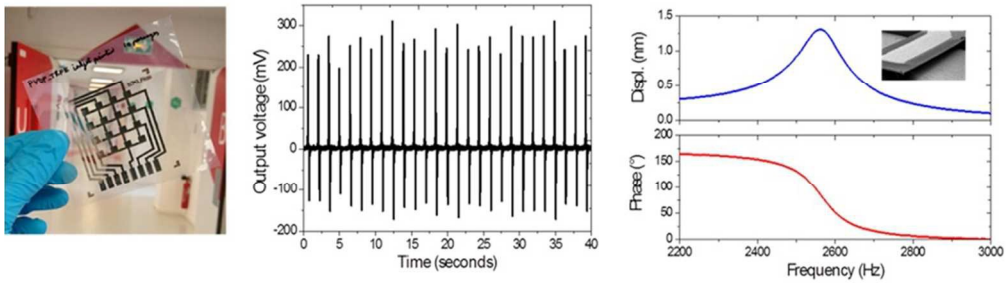


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